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Seasonal flow, nutrient concentrations and loading patterns in stream flow draining an agricultural hill-land watershed

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Abstract

The effects of seasonality on nutrient patterns and export in streamflow were determined for a 7.3 km^2 agricultural hill-land watershed in Pennsylvania for a 12-year period, 1984–96. Dissolved phosphorus (DP) concentrations were highest in stormflow for all seasons (0.030 mg l^{-1}), especially summer (0.039 mg l^{-1}) when the flow was the least. About two-thirds of the DP export was in stormflow, with two-thirds of this export occurring during winter and spring when five of the seven largest stormflow events within a year occur. For larger stormflows, DP concentrations were positively correlated with the flow rate, which contributed to storm dominance of DP export. Export of NO_3-N, and to a lesser extent DP, by flow component and season were controlled by flow rate rather than concentration. Summer was least important, contributing only 7–8% of the annual export of water, DP, and NO_3-N. The NO_3-N concentrations were the lowest for the baseflow (5.36 mg l^{-1}) and the highest for the elevated baseflow (7.12 mg l^{-1}) across seasons. More of the NO_3-N export was in non-stormflow than stormflow and occurred mostly in winter and spring. One 50-year return period storm event generated a substantial portion (9%) of the DP exported for the 12-year period of the record, but had much less impact on water (2%) and NO_3-N (1%) export. P management and control decisions for watersheds need to be developed in a storm-based, source-area framework, whereas N management and control decisions depend more on managing and balancing N use over the watershed. Published by Elsevier Science B.V.

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1. Introduction

Seasonality is important for selecting the proper sampling, simulation and remedial strategies for controlling nutrient export from watersheds (Alberts et al., 1978; Foster, 1978). For watersheds where climatic conditions, biomass productivity, and land use activity and management change substantially from season to season, this effect can be major (Alberts et al., 1978; Owens et al., 1991, 1992). For many agriculturally dominated watersheds, in the humid northeastern US, up to one-half of the annual precipitation passes through the watershed into streamflow. Depending on the season, the sources of this streamflow and their impacts can vary. During winter, under fully recharged hydrologic conditions, streamflow may be primarily subsurface discharge originating from multiple strata and the expanded contributing areas within the watershed. During summer, surface runoff from very small areas and subsurface discharge originating from deeper strata over the whole watershed may dominate streamflow.

Watershed WE-38, located in east-central Pennsylvania, is the subject of much research on nutrient and

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hydrologic source areas contributing to streamflow. Hydrologically, WE-38 is a variable source area (VSA) watershed, which means the primary surface runoff zone is close to the stream and dynamic, i.e. it expands rapidly and substantially upslope in response to the large storms (Gburek, 1990). Basically, the VSA exists because the groundwater table approaches the land surface near the stream, causing seep zones and the high soil moisture condition for its rapid expansion upslope.

In a recent study (Pionke et al., 1996), dissolved orthophosphorus (DP), total dissolved phosphorus (DP plus polyphosphorus and organic P), and nitrate (NO_3-N) export patterns in streamflow from WE-38 were determined and summarized for a nine-year period (1984–1993). Total flow, categorized by each flow component was: baseflow 28%; elevated baseflow 26%; and stormflow 45%. Algal-available P accounted for 57% of the total P exported, of which about half was sediment-associated and half was DP (Pionke and Kunishi, 1992). Most of this DP (70%) and algal-available P (90%) was exported during storm flow, being dominated by the seven largest flow events each year (Pionke et al., 1996, 1997). Nearly all nitrogen (N) exported in streamflow is as NO_3-N (Pionke and Urban, 1985; Schnabel et al., 1993). About 65% of the NO_3-N was exported during non-storm periods as baseflow and elevated baseflow. Stormflow accounted for 35% of NO_3-N export based on high frequency (2.8–11.3 min) samplings of 61 storm hydrographs, and for 50% based on a routinely sampled (3/wk) nine-year data set (Pionke et al., 1996). This 15% discrepancy and surprisingly large NO_3-N export by stormflow results from the fact that subsurface return flow, containing high NO_3-N concentrations, dominate major portions of the storm hydrograph (Pionke et al., 1988, 1993).

Some research on seasonal effects related to nutrient export has been done in WE-38 and observed in largely agricultural watersheds for similar climates. Gburek and Heald (1974) observed soluble P concentrations (HCl extractable from 0.45 μm filtrate) of WE-38 streamflow from 1969–71 to be about twice as high in summer when compared with that in the rest of the year. Most soluble P export (60 + %) occurred from February–March or April and resulted from high flow events. Owens et al. (1991) found NO_3-N concentrations and export in both baseflow and stormflow from a 32-ha Ohio hill-land watershed to be lowest in summer and highest in winter. Averaged over four small (18–123 ha) forested and mixed forested-agricultural watersheds, they found two-thirds of the total P and one-half of the NO_3-N exported annually to be in stormflow. For very small ($<$ 1 ha) pastured watersheds that received substantial application of fertilizer N (168 kg ha^{-1}), Owens et al. (1992) found the highest stream NO_3-N outflow rates and concentrations to occur in February to April, especially February, and the lowest rates and concentrations to occur from August to October. They found the basic seasonal pattern described in their 1991 work to occur irrespective of land use and management, although the NO_3-N winter peak appeared to be slightly delayed in the much smaller N-fertilized pastured watersheds than in mixed forested-agricultural watersheds (Owens et al., 1992).

More work has been done on forested systems in similar climates, but the results are highly variable. For example, using a 13-year data record from a 126-ha watershed located in New Hampshire, Meyer and Likens (1979) observed export of dissolved phosphorus, determined by persulfate digestion of the filtrate, to peak twice, once in April–June and to a lesser extent in November–December, with two minimums in August–October and January–March. DeWalle and Davies (1997) examined data from 13 large watersheds (0.9–23 km^2) in the northeastern US, and observed the NO_3-N concentration in streamflow to peak from January to March, typically in February. The peak NO_3-N concentrations observed in January–March for the 13 larger forested watersheds match up with the NO_3-N concentration and export patterns shown by Owens et al. (1991, 1992) for mostly agricultural watersheds. Murdoch and Stoddard (1992) observed the highest NO_3-N concentrations and export to occur in late autumn through early spring and the lowest to occur in summer over a 7-year record collected from a 9.9 km^2 forested watershed in New York. Among the forested watersheds, this matched up best with Owens et al. (1991, 1992). However, Mulholland and Hill (1997) showed NO_3-N and DP concentrations in streamflow to be highest in summer with two minima in early spring and late autumn, for two small Tennessee hill-land watersheds. These very different timings observed in different forested watershed studies may result from the nutrient and litter cycling of forested systems. Their very low nutrient status can cause minor components of the nutrient cycle and precipitation input of N to exert controls (Murdoch and Stoddard, 1992) that typically would be overwhelmed in a more nutrient-rich and better nutrient-buffered agricultural watershed.

Seasonality of nutrient export and concentration in streamflow is subject to some basic controls. Climate establishes the seasonality of flow and stormflow, which controls nutrient export patterns. Nutrient availability and supply affect the seasonality of nutrient concentration in this export, and the characteristic concentration difference is tied to flow origin. Nutrient availability and supply on agricultural watersheds can vary seasonally as a function of biomass mineralization-immobilization patterns, and the timing of manure and fertilizer application (Foster, 1978). As we attempt to better sample, model, and control nutrient export from watersheds, we need to address seasonality.

The objectives of this paper are: (1) to determine the seasonal effects on DP and NO_3-N concentration and export patterns by streamflow component, and (2) to study the impact of a single large storm event on these patterns. The nine-year data set analyzed and reported by Pionke et al. (1996) was expanded to 12 years and brought up-to-date. in order to examine the seasonality effects, especially, by flow component and the impact of the extreme event.

2. Experimental design, sampling and analysis

The WE-38 watershed and hydrograph sampling-classification technique were described in Pionke et al. (1996). The following summarizes this information, and the sampling, analytical, and data processing methods where similar. Altered or additional methodologies are presented in detail.

2.1. Watershed description

Watershed WE-38, also referred to in the past as the MCR Watershed, is located approximately 40 km north of Harrisburg, PA, within the Susquehanna River Basin (Pionke et al., 1996). The average hydrologic budget (mm y^{-1}) determined from 1983 to 1988 for this 7.3 km^2 watershed was: precipitation 1164; evapotranspiration 577; streamflow 587, with stormflow accounting for about 20% of the streamflow. Precipitation is nearly uniform, if calculated on a monthly basis (Gburek, 1977). This watershed is 57% cropland, 35% forest, and 8% permanent pasture and contains no urban, industrial, or coal mining areas. Major farming activities are mostly cash cropping, with some livestock production carried out on family farms. Geology, topography, and soils typify the unglaciated, intensely folded and faulted Valley and Ridge Province of the Appalachian Highlands.

2.2. Sampling and analysis

Samples were collected routinely by hand two to three times weekly at a continuously gauged weir at the watershed outlet from 12/23/83 to 3/8/96. This data set was used to develop the time-averaged and flow-weighted summaries by flow component and season used in all figures and tables. Because relatively few samples contained sediment, this sediment was discarded and not analyzed. The data set provides concentrations and loads for the water phase only.

Once collected, the samples were immediately iced down, stored at 3°C, filtered (0.45 μm) within one week, and analyzed within three weeks. Water samples were analyzed directly for orthophosphate (DP) using a colorimetric ascorbic acid method (US Environmental Protection Agency, 1983). NO_3-N was analyzed directly by a Waters IL/C Ion Chromatograph[1] using standard procedures. DP concentrations can be used to estimate total dissolved phosphorus (TDP) concentrations using the equation, TDP $=$ 0.001 $+$ 1.21DP, derived from this sample data set for DP concentration ≥ 0.010 mg l^{-1} ($n = 578$, $r^2 = 0.873$, $P < 0.0001$). TDP was analyzed similarly to DP following persulfate digestion (US Environmental Protection Agency, 1983) of the filtered sample and is the sum of DP, polyphosphorus, and organic phosphorus.

2.3. Data classification, grouping, and analysis

The data were categorized both by season and flow component. The seasons were January–March

[1] The mention of trade names in this publication does not constitute an endorsement of the product by the USDA over other products not mentioned.

Table 1
Summary of flow, dissolved P, and NO_3-N concentrations by flow component and season for the WE-38 Watershed, 1984–1996. In this table, DP is dissolved orthophosphate; *x* is mean; sd is standard deviation; *m* is median; qr is quartile range defined as 75% minus 25% value. Baseflow refers to samples from long-term stable low flow periods. Elevated baseflow refers to samples from shorter-term or seasonal higher-flow nonstorm periods. Stormflow refers to samples from storm hydrographs. Of this data 2.2% could not be classified by the flow component and were excluded. Seasonal means not followed by the same lowercase letter, and flow component means not followed by the same uppercase letter, are significantly different at the 1% level of probability. Significance for flow and DP were assessed on a log transformed scale

Season	Flow ($l\ s^{-1}$)			DP ($mg\ l^{-1}$)			NO_3-N ($mg\ l^{-1}$)		No. of observations
	x	*m*	qr	*x*	*m*	qr	*x*	sd	
All									
Jan–Mar	197a	94	153	0.012a	0.009	0.007	6.35a	1.37	320–325
Apr–Jun	178a	81	143	0.011a	0.009	0.012	5.54b	1.97	418–428
Jul–Sep	41b	18	23	0.016b	0.014	0.013	4.60c	2.02	393–407
Oct–Dec	131c	56	106	0.011a	0.008	0.007	7.04d	2.26	335–367
Total	134	56	112	0.012	0.010	0.010	5.81	2.14	1469–1527
Baseflow									
Jan–Mar	80a	70	58	0.010a	0.008	0.006	6.17a	1.21	214–217
Apr–Jun	73a	53	66	0.009a	0.008	0.010	4.94b	1.27	295–299
Jul–Sep	23b	16	17	0.014b	0.014	0.012	4.28c	1.75	317–330
Oct–Dec	52c	37	48	0.007a	0.007	0.007	6.58a	2.08	236–257
Total	55A	39	59	0.010A	0.008	0.011	5.36a	1.86	1063–1103
Elevated baseflow									
Jan–Mar	260a	221	168	0.011a	0.011	0.006	7.00a	1.61	68–69
Apr–Jun	253b	206	175	0.011a	0.011	0.007	6.91a	2.40	78–80
Jul–Sep	83c	63	95	0.019a	0.016	0.016	6.21a	2.25	55–56
Oct–Dec	182b	170	141	0.013a	0.011	0.008	8.39b	2.10	60–68
Total	203B	129	169	0.013B	0.011	0.008	7.12B	2.23	262–273
Stormflow									
Jan–Mar	735a	617	682	0.027a	0.026	0.016	6.22ab	1.41	38–39
Apr–Jun	694a	576	721	0.029a	0.022	0.029	7.08ab	2.78	45–49
Jul–Sep	202b	127	209	0.039a	0.028	0.025	5.23a	3.03	21–21
Oct–Dec	527a	410	739	0.028a	0.020	0.020	7.76b	2.56	39–42
Total	590C	442	690	0.030C	0.023	0.022	6.76B	2.58	144–151

(Winter), April–June (Spring), July–September (Summer), and October–December (Autumn). This seasonal grouping was not objectively selected, but instead was selected to divide the year into four equal time periods, while basically grouping periods of similar flow according to flow levels observed in this and earlier data sets. The flow components were baseflow, elevated baseflow, and stormflow. Sample placement into these categories is shown in Fig. 2 of Pionke et al. (1996), and is summarized as follows.

Samples taken during: (1) the rise, peak, or very early recession of a storm hydrograph were classified as stormflow; (2) stable non-stormflow (for example, high flow rates if typical, such as during later winter) or extended stormflow recession periods (usually at least two days past the hydrograph peak) were classified as baseflow; (3) post-storm drain-down period, usually less than two days following the hydrograph peak and characterized as atypical, relative to the extended baseflow recession, were classified as elevated baseflow. Thirty-four of the 1562 samples collected could not be classified and were deleted from the flow data set. The total data set used for most of the paper excludes one sample representing an extreme event. This sample, taken on 19 January 1996, represented the flow peak resulting from a major rainstorm on a ripe snow pack. The flow rate ($23\ m^3\ s^{-1}$) exceeded the next largest flow rate associated with any sample by 10 times and provided abnormally high DP ($0.095\ mg\ l^{-1}$), and moderately low NO_3-N ($4.00\ mg\ l^{-1}$) concentrations.

The flow volume and nutrient loads, presented seasonally or totally and by flow component, were estimated by computing the volume or load produced over the sampling interval, and then summing up the appropriate sampling intervals. The flow rate ($l\,s^{-1}$) and nutrient concentrations ($mg\,l^{-1}$) measured at the time of sampling were assumed constant over the sampling interval, usually one-third of a week (56 h). The effect of the 19 January 1996, extreme event was added in as a 32-hour sampling interval, where flow volume was computed from a 32-hour hydrograph which was sampled once during the flow peak.

All data was checked for normality, and because flow and DP exhibited log-normal distributions, analysis of variance procedures for these variables were computed on log-transformed data. Tukey's studentized range test, with the Tukey–Kramer modification for unequal sample sizes (SAS Institute Inc., 1998) was used to compare all pairs of means following analysis of variance. About 22% of all DP concentrations were below the practical quantitation limit (PQL) (Gibbons, 1994) which never exceeded $0.005\,mg\,l^{-1}$ P over the period of record. In terms of flow categories, DP concentrations below the PQL were 26% for baseflow, 15% for elevated baseflow, and 5% for stormflow. For these samples, PQL ÷ 2 was used in all calculations.

3. Results and discussion

The data set was summarized and analyzed using three approaches. The first explores the values and distribution by flow component and season for the time-averaged data. Because the samples were collected at a set frequency over the 12 years of record, the sample means by all categories were time-averaged. The second presents and examines chemical export obtained by flow weighting. The third examines how a single large storm affected both time-averaged and flow-weighted values and patterns.

3.1. Patterns in flow rate, DP, and NO_3-N concentrations

As expected, the patterns, concentrations, and frequency histograms for flow, DP, and NO_3-N overall and by flow component for the 12-year data were similar to the nine-year data set (Pionke et al., 1996). All flow data and the DP in total flow and baseflow exhibited a log-normal distribution. DP in stormflow and elevated baseflow, along with some seasonal subgroups in these two flow categories, tended toward normal distributions. The bias toward the log-normal distribution was greatest for baseflow and the baseflow-dominated total flow subgroups, in part because this baseflow sample population is enriched (26%) with DP concentrations at the PQL ($0.005\,mg\,l^{-1}$ P). In contrast, the NO_3-N distributions by flow component and season were approximately normal.

The stormflow rate on an annual basis was about 10 times the baseflow and three times the elevated baseflow rates (Table 1). These flow rates were highly variable as shown by the quartile range (75–25% value), but the means were significantly different ($P < 0.01$). Subdividing the total data set by season and repeating this analysis did not change these results, suggesting that the relationship between flow components for the total data set was consistent and stable across seasons. The sample occurrence by flow component for the 12-year vs. the nine-year data set was similar: baseflow 70.6 vs. 67.1%; elevated baseflow 17.5 vs. 19.3%; stormflow 9.7 vs. 10.8%; unclassified 2.2 vs. 2.8%, respectively.

The flow rate by season followed a major and minor pattern. For the three flow components as well as the total data set, the July–September mean rates ranged from one-third to one-fourth of those from the other three periods. Among the other three periods, the seasonal flow rate patterns by flow component were consistent (January–March > April–June > October–December), but the differences between the means were not statistically significant ($P < 0.01$) except for baseflow in October–December.

Mean annual DP concentrations were about three times higher for stormflow than that for either baseflow or elevated baseflow (Table 1). This difference was significant ($P < 0.01$). Overall, the mean seasonal DP concentrations followed a simple pattern; the July–September concentration consistently exceeded those from the other three periods, whether organized by flow component or for the total flow data set (Table 1). These differences ranged from being statistically significant ($P < 0.01$) for total flow and baseflow to non-significant for stormflow. Otherwise, DP concentrations changed very little between the other seasons.

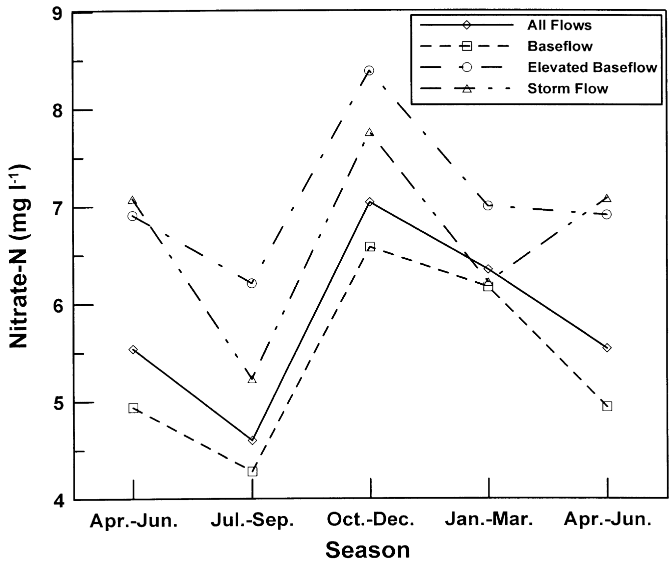

Fig. 1. Mean Nitrate-N concentration by flow component and season.

The variability in DP, expressed as the quartile range, was high, often approaching the mean and sometimes exceeding the median, whether the data was examined by flow component, season, or both.

Mean annual NO_3-N concentrations were lowest in baseflow and highest in elevated baseflow (Table 1). The baseflow mean was significantly different ($P < 0.01$) from both elevated baseflow and stormflow means. The reason that stormflow had high NO_3-N concentrations was because storm hydrograph samples, even for major events, consisted of 40–95% subsurface return flow (Pionke et al., 1993). Mean seasonal NO_3-N concentrations followed a more complex pattern (Table 1). For all flow categories, the highest concentrations were in October–December, and the lowest were in July–September (Fig. 1). Although the mean NO_3-N concentrations differed greatly among flow components, the increase in NO_3-N concentrations from summer to autumn were surprisingly consistent in magnitude (2.2–2.5 mg l^{-1}). These increases and the differences in NO_3-N concentrations by flow component during summer and fall were significant ($P < 0.01$).

There appeared to be two predictable and stable controls on NO_3-N concentrations. The first was characteristic of the flow component and reflected the N status and position of its dominant flow sources in the watershed. The second was the seasonal progression in soil moisture from a summer deficit to an autumn excess with drainage causing the remobilizing of stored soil NO_3-N, and the expansion of hydrologic source-areas for all flow components. The mean flow rate (l s^{-1}) change from summer to autumn (baseflow 23 to 52; elevated baseflow 83 to 182; stormflow 202 to 527) expressed as % increase (126, 119 and 161, respectively) was similar irrespective of flow component. However, from autumn to winter the differences in NO_3-N mean concentration among flow components decreased by 1.8 to 0.8 mg l^{-1} (Fig. 1) and were not significantly different ($P < 0.01$), suggesting greater similarity in the sources and controls on NO_3-N concentrations in winter, irrespective of flow component. The six-month winter to summer transition period showed variable response in NO_3-N concentrations depending on the flow component (Fig. 1). For baseflow, the concentrations were highest in autumn and winter, and lowest in spring and summer. For elevated baseflow, NO_3-N concentrations were much higher in autumn, being substantially lower and most similar in winter and spring. For stormflow, winter and spring concentrations were similar, with summer (lowest concentration) and autumn (highest concentration) being statistically different ($P < 0.01$).

Table 2
Distribution of outflow volume and nutrient load exported from the WE-38 watershed by flow component and season (computed as % of flow component)

Parameter	Flow component	Seasons				
		All (%)	Jan–Mar (%)	Apr–June (%)	July–Sept (%)	Oct–Dec (%)
Flow	Total[a]	100	36	33	7	24
	Base	29	10	10	2	7
	Elevated base	27	10	9	2	6
	Storm	44	16	14	3	11
NO_3-N Load	Total	100	36	30	7	27
	Base	26	9	8	2	7
	Elevated base	30	11	9	2	8
	Storm	44	16	13	3	12
DP load	Total	100	34	32	8	26
	Base	16	5	5	2	4
	Elevated base	18	6	6	1	5
	Storm	66	23	21	5	17

[a] Sum of the baseflow, elevated baseflow, and stormflow—excludes unclassified flows.

With respect to seasonality, the dominant feature was the consistently much lower mean flow rates and higher DP mean concentrations in the summer period for baseflow, elevated baseflow, and stormflow. The NO_3-N seasonal patterns were much more complex, with NO_3-N concentrations being lowest in summer and highest in autumn for each flow component. Moreover, NO_3-N mean concentrations differed among flow components across seasons, being highest in elevated baseflow, lowest in baseflow, and intermediate for stormflow. However, all flow components tended toward a common NO_3-N mean concentration in winter, these not being significantly different ($P < 0.01$). From summer to autumn, the NO_3-N mean concentration increased dramatically and similarly across all flow components.

3.2. Patterns in outflow volume, DP and NO_3-N export

Although stormflow occurred only 10% of the time, it accounted for 44% of the total outflow volume (Table 2). Baseflow occurred 72% of the time, accounting for 29% of the volume, and elevated baseflow occurred 18% of the time, accounting for the remaining 27%. Summer accounted for only 7% of total outflow; over two-thirds of the total outflow occurred during the first half of the year. The flow components showed the same seasonal pattern as did total flow.

The pattern of NO_3-N export by flow component and season was similar to the pattern of water flow (Table 2). In fact, outflow volume was the primary control on NO_3-N export because flow rates can vary by multiples or an order of magnitude, whereas the corresponding NO_3-N concentrations shown in Table 1 varied by only small percentages. Moreover, the NO_3-N concentrations for all samples, when stratified and then averaged by flow interval, changed very little from 50 to 3000 $l\,s^{-1}$ [Fig. 7 in Pionke et al. (1996)], showing the NO_3-N sources in this watershed not to be limiting or diluted even when subject to very high flow conditions. Very little of the NO_3-N was exported during the summer (7%). The soil water and ground water recharge period starting in autumn and ending in late spring exported most of the NO_3-N from this watershed, with the greatest seasonal export occurring in winter.

Baseflow and elevated baseflow together exported the most NO_3-N (56%) (Table 2). However, stormflow was the most important single flow component, accounting for 44% of annual export. In a similar climate, topography and land use, Owens et al. (1991) found 47–67% of the annual NO_3-N load exported in stormflow from watersheds. Where precipitation excess is the dominant component of surface runoff and controls stormflow, we would expect this stormflow to export substantially less NO_3-N. NO_3-N concentration of rainfall sampled at WE-38 over a 10-

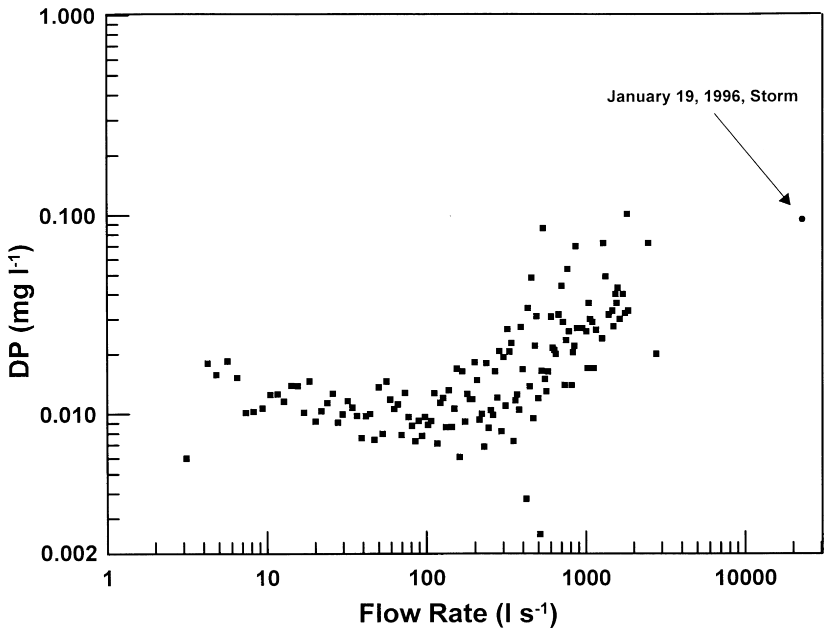

Fig. 2. Relationship between DP concentration and flow rate.

year period averaged less than 0.5 mg l^{-1}. However, the WE-38 storm hydrographs were often dominated by the subsurface return flow component which can range from 40–95%, and was mostly above 80% (Pionke et al., 1993). Near-stream seep zones and high water tables, the primary source of this quick subsurface return flow, contained high NO_3-N concentrations (Pionke et al., 1988; DeWalle and Pionke, 1994). Also, Pionke et al. (1996) showed that stormflows represented by single samples collected routinely over a long-time period contained about twice the NO_3-N concentration (6.97 vs. 3.78 mg l^{-1}) than did those discharge-weighted from high frequency samplings over storm hydrographs. The relatively close agreement between the time-averaged (6.76 mg l^{-1}) compared to the discharge-weighted (7.48 mg l^{-1}) NO_3-N concentrations computed for stormflow, based on three-times weekly sampling over 12 years, showed this large difference in NO_3-N concentration (6.97 vs. 3.78 mg l^{-1}) to be real, not just an artifact introduced by the choice of sample weighting method. In WE-38, the surface runoff component can be sufficiently large and low in NO_3-N concentration to greatly reduce the NO_3-N concentrations of peak flow (Fig. 2 of DeWalle and Pionke (1994); Fig. 3 of Pionke et al. (1988)). This is difficult to sample without using a hydrograph based sampling strategy. As a result, the 32.6% of the NO_3-N exported by stormflow reported earlier (Pionke et al., 1996) is more realistic than the 44% presented here, but this 44% is the best result obtainable using a routine sampling schedule rather than a combined routine schedule and event-based sampling scheme.

The DP was exported mostly in stormflow (66%) and then mostly during January–June (44%) (Table 2). Previous work (Gburek and Heald, 1974; Pionke et al., 1996) and Table 1 showed highest DP concentrations to be associated with stormflows. Pionke et al. (1996) showed DP concentrations to remain approximately constant across flows ranging from about 25 to 250 l s^{-1}, but to increase with flow rate above 250 l s^{-1}. This figure was replotted with 12 years of data where each data point represents the mean DP value at a flow rate (Fig. 2). For lower flow rates, means included up to 40 samples. At the higher flow rates, many means represented single samples. The relationship appears continuous and curvilinear except the increase in DP concentrations with increasing flow rate started much lower (100 l s^{-1}). Moreover, the larger storms become progressively more important in controlling DP export. From the nine-year data set, Pionke et al. (1997) noted that 70% of the DP and 90% of the DP plus bioactive sediment P (Pionke and Kunishi, 1992; Pionke et al., 1996) annual loads were exported by the seven largest storms. Based on the 70 largest storm samples ($>500\ l\ s^{-1}$) collected over the 12 years, their distribution by season was: winter 31%; spring 40%; summer 3%; autumn 26%. Five of these seven largest storms occurred during the January–June period, which is also the period when two-thirds of all DP was exported.

Knowing which flow components, storm characteristics, and season dominate P export provides very useful information for sampling, predicting, and managing P export. Most surface runoff occurs from relatively small areas (VSA) located near streams. Storm size and its timing relative to the initial hydrologic condition of the watershed (a function of seasonality) affects the development and extent of these VSAs. It provides a logical basis to select those storm(s) and initial condition(s) that control DP export, and to use this information to better assess and identify source areas and the most effective and cost-efficient remedial strategies. The NO_3-N export is well distributed between baseflow, elevated baseflow, and stormflow overall and by season. Unlike P export, which is concentrated in time (10% occurrence), space (VSAs), storm characteristics (seven largest storms), and hydrologic status (January–June), NO_3-N export is more dispersed. As a result, the sampling, assessment, and control of NO_3-N export are likely to be more focused on the N management issues, such as “how much,” N is input by “what” activities rather than on “when” and “where” these inputs and activities occur.

3.3. Impact of an extreme event on flow rate, concentrations, and nutrient export

A major runoff event occurred from 19–29 January 1996, resulting from melt of a snow pack augmented by several rain storms. During this period, four samples were taken, one during the major flow peak occurring on 19 January at the beginning of the snow melt sequence, when 58 mm of rain fell on a well-ripened snow pack (394 mm depth, 29% water content) in 19 h, generating a peak flow rate of $23\ m^3\ s^{-1}$. The other three samples were excluded from the computation because they do not represent stormflow (range from 400 to $1400\ l\ s^{-1}$, 0.011–0.020 mg l^{-1} DP, 6.50–6.70 mg l^{-1} NO_3-N, mostly from snow melt). The $23\ m^3\ s^{-1}$ flow rate exceeded by 10 times the next largest flow rate among the 1527 samples that make up the 12-year data set used in this paper (Fig. 2). The NO_3-N and DP concentrations were very different (4.00 and 0.095 mg l^{-1}, respectively) from the corresponding mean stormflow values (6.76 and 0.030 mg l^{-1}) given in Table 1. The storm plus snow-melt event represented by this sample was computed based on the peak flow rate to have 65-year streamflow (Flippo, 1997) and 50-year rainfall (Pennsylvania Department of Environmental Resources, 1983) recurrence intervals. Two events with larger peak flow rates (24.9 and $24.1\ m^3\ s^{-1}$) occurred during summer, 1986, however, flow volumes were only a small fraction (8%, 27%) of this event. Using a flow-rate boundary of $2500\ l\ s^{-1}$ to define the storm hydrograph, this storm yielded 10^9 l of outflow in 32 h or the equivalent of 137 mm water depth over the watershed. Our goal was to analyze the impact of this single storm sample on the results from the full year and January–March total flow and stormflow categories.

In terms of flow, this single sample increased the mean flow rate for the 12-year total flow record by only 2% (Table 3). However, in the stormflow category for January–March, it increased the mean flow rate and water volume exported by 14%. Impacts on the mean chemical concentrations for the total flow, total stormflow, and January–March stormflow records were negligible because of the large number of sample observations. The greatest impact was on the DP export which increased 9%, mostly due to the increased DP concentrations (0.095 vs. 0.012 mg l^{-1}). In contrast, the substantially reduced NO_3-N concentration (4.00 vs. 5.81 mg l^{-1}) caused this major storm to increase the NO_3-N exported by only 1%. Considering that this is a long- term record (12 years) taken from a relatively large experimental watershed in a humid, temperate climate where high flow rates and large outflow volumes are typical, this single sample accounted for 9% of the total DP exported over the 12-year record, and 14% of the outflow volume and 26% of DP exported in stormflow during January–March. The results show: (1) the impact of including or

Table 3
Comparison of flow rates, nutrient concentrations, and nutrient loads exported with and without largest storm (19 January 1996). This rainfall on snowpack storm generated ten times (23 $m^3 s^{-1}$) more runoff than the next largest storm sample in the 12-year record[a]

	Total flow		Storm flow	
Parameter	All year	Jan–Mar	All year	Jan–Mar
Flow				
Mean ($l s^{-1}$)	137(134)	208(197)	616(590)	839(735)
Volume (%)	+2(100)	38(36)	45(44)	18(16)
DP				
Mean ($mg l^{-1}$)	0.012(0.012)	0.012(0.012)	0.030(0.030)	0.029(0.027)
Load (%)	$+9^b$(100)	40(34)	69(66)	29(23)
NO_3-N				
Mean ($mg l^{-1}$)	5.81(5.81)	6.34(6.35)	6.74(6.76)	6.17(6.22)
Load (%)	$+1^b$(100)	37(36)	45(44)	17(16)

[a] Numbers in brackets denote the results of Tables 1 and 2, which do not include the 19 January 1996 storm.
[b] Here the % of change = 100 × (10^9 l × nutrient concentration in storm sample) ÷ (134 $l s^{-1}$ × discharge weighted nutrient concentration for the 1527 samples × seconds per 12 years) where discharge-weighted NO_3-N = 7.01 $mg l^{-1}$, DP = 0.021 $mg l^{-1}$.

excluding a single dominating event; and (2) the importance of examining a data set and establishing guidelines for including and excluding samples in accordance with project objectives before proceeding with analysis.

4. Summary and conclusions

The flow rate pattern was stable and predictable whether organized by flow component, season, or both. The stormflow rate was about 10 times greater than the baseflow rate and about three times greater than the elevated baseflow rate. This 10:3:1 pattern held across seasons even though the flow rates decreased markedly from spring to summer and increased markedly from summer to autumn. The summer flow rates, irrespective of flow component, were about one-third to one-fourth those for autumn, winter, and spring. There was a tendency for flow rate, especially baseflow, to be less in autumn than winter, likely because the soil water and storage deficit was being refilled following summer, causing groundwater levels in the watershed to peak during winter which would support the high baseflow and elevated baseflow discharge rates.

The DP concentration pattern was less clear than the flow rate pattern, but showed consistency. Stormflow concentrations exceeded both baseflow and elevated baseflow concentrations by about three times. This 3:1:1 pattern held across the four seasons. The summer concentrations, irrespective of flow component, were always greatest, thus matching the seasonally-highest DP concentrations with the seasonally-lowest flow rates. Although important in terms of DP concentration in summer streamflows, the effect of these seasonally-highest DP concentrations on DP export was very small.

The NO_3-N concentration pattern showed consistencies, but was seasonally more complex than for DP. NO_3-N concentrations were about 1.5 $mg l^{-1}$ less in baseflow compared to the elevated baseflow and stormflow. Although this pattern generally held across seasons, there was a seasonal pattern superimposed. One seasonal change was the summer dry-down through autumn recharge period when the NO_3-N concentrations by flow components increased greatly (2 $mg l^{-1}$) and similarly. Following this period, the flow components tended to merge and mix during winter, before separating back into their spring to summer patterns. The increasing soil and groundwater recharge from late summer to winter first activates processes in the flow-depleted watershed to generate more flow from flow-component sources, which then progresses more to mixing and merging of flows irrespective of their sources. The highest NO_3-N concentrations in elevated baseflow and lowest NO_3-N concentrations in baseflow support the concept of a two-layer fractured rock drainage system operating on this watershed (Schnabel et al., 1993; Gburek et al., 1999). The elevated baseflow is dominated more by the shallow layer, which directly underlays most of the agricultural area, and fills mostly during autumn and drains mostly during spring. The deeper groundwater layer contains more drainage from the N-limited ridge-top forests (Pionke and Urban, 1985).

The stormflow NO_3-N concentrations are likely overestimated because sampling is biased to the subsurface discharge component of the storm hydrograph. Previous work showed stormflow NO_3-N, determined from intensive sampling over 61 hydrographs, to be about half that using the current technique. The problem is one of sampling frequency, not a sample data averaging (discharge vs. time) issue. On this and similar watersheds, most of the storm hydrograph is dominated by subsurface return flow. The surface runoff period, which can be very intense and produce large volumes with low NO_3-N concentrations, is short compared to the total storm hydrograph. The result is that even with great care, having access to hydrographs and large routinely-collected data sets, both the NO_3-N concentration and export by stormflow is likely to be overestimated. For smaller watersheds with continuous flow records, inadequate sampling of the high flow-low NO_3-N storm component could cause overestimations of the NO_3-N concentration and export. This could underestimate the storm-based DP export as well.

Export of water, NO_3-N, and DP from the watershed were basically similar when organized by flow component, season, or both. In large part, this reflects the dominant role of flow in nutrient export. Stormflow was the single largest source of streamflow. Although stormflow accounted for about two-thirds of exported DP, baseflow plus elevated baseflow accounted for the majority of exported NO_3-N. Considering the sampling bias to the subsurface sources of stormflow, the sum of this stormflow, baseflow, and elevated baseflow exports considerably more NO_3-N, perhaps as much as three-fourths of the total. The NO_3-N concentrations tended to be similar and not diluted over the full range of flows, suggesting that NO_3-N sources in this watershed are not limiting export. With respect to seasonality, nearly 70% of the water, NO_3-N, and DP export occurred during winter and spring, with only 7–8% occurring during summer.

The effect of stormflow on P export is multiplicative, because DP concentration and the erosion-sediment transport potential progressively increase with storm size. For example, a $1000\ \mathrm{l\ s^{-1}}$ stormflow will export about 12 times as much DP as a $200\ \mathrm{l\ s^{-1}}$ stormflow. In a previous study, we noted that 70% of DP and 90% of the DP plus bioactive sediment P was exported each year mostly by the seven largest storms (Pionke et al., 1997). Five of these seven storms occurred during winter and spring. Rarely do these larger storms occur in summer.

Because P export is concentrated in time (10% occurrence), space (VSAs), by storm characteristic (seven largest storms) and during the most storm prone and wettest initial conditions (January–June), we can use this information to better delineate sources and to better design sampling, assessment, and remedial methods. In contrast, NO_3-N export is much more dispersed in time, space, and by flow component. The result is that N use, balance, and management over the longer term, and the watershed, may be the most realistic targets for controlling N export.

The impact of a single outlier storm can have a great effect on export. A single storm with 50-year rainfall and 65-year streamflow recurrence intervals accounted for 9% of the DP exported from this watershed over a 12-year period. The effect on seasonal export was much larger. The effect on NO_3-N export was negligible (1%). The dilemma is that storms this large generate so much flow over a few days, that it is difficult to assess the impact of this exported load on downstream water quality. Clearly, such large events can hydraulically disrupt and even flush out downstream lakes and estuaries, which means this nutrient export may have an entirely different impact than that exported during the rest of the record. Also, such large events cause most of the watershed to become a source area, which overwhelms the conventional land-based controls and remedial approaches. When using long-term data sets, such dominating events will appear. The decision of whether to exclude or include them when doing nutrient export evaluations is not trivial and depends on the goals of the analysis.

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